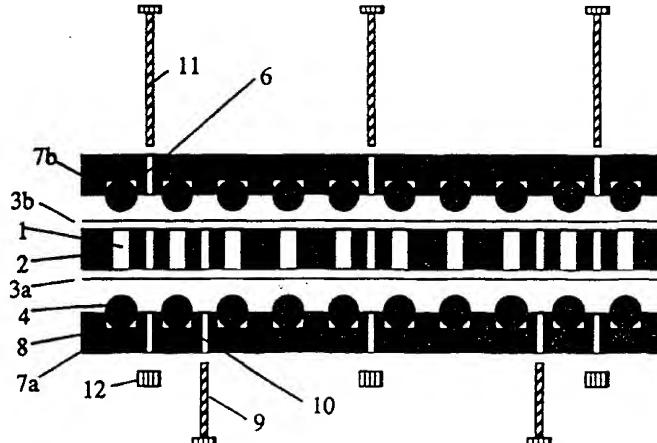




INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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| (51) International Patent Classification 6 : B01J 3/00, C30B 29/34 | A1 | (11) International Publication Number: WO 98/36826 (43) International Publication Date: 27 August 1998 (27.08.98) |
| <p>(21) International Application Number: PCT/NO98/00051</p> <p>(22) International Filing Date: 20 February 1998 (20.02.98)</p> <p>(30) Priority Data: 970788 20 February 1997 (20.02.97) NO</p> <p>(71) Applicant (for all designated States except US): SINVENT AS [NO/NO]; Strindveien 4, N-7034 Trondheim (NO).</p> <p>(72) Inventors; and</p> <p>(75) Inventors/Applicants (for US only): WENDELBO, Rune [NO/NO]; Peer Gyntsv. 2, N-0854 Oslo (NO). AKPORIAYE, Duncan, E. [NO/NO]; Kristine Bonnevies vei 15, N-0592 Oslo (NO). KARLSSON, Arne [NO/NO]; Grågåsveien 1c, N-1187 Oslo (NO). DAHL, Ivar, Martin [NO/NO]; Kongsberggata 6, N-0468 Oslo (NO).</p> <p>(74) Agent: BENDIKSEN, Asbjørn; Bryn & Aarflot a/s, P.O. Box 449 Sentrum, N-0104 Oslo (NO).</p> | | <p>(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, GW, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).</p> <p>Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p> |

(54) Title: MULTIAUTOCLAVE FOR COMBINATORIAL SYNTHESIS OF ZEOLITES AND OTHER MATERIALS



(57) Abstract

The invention relates to a multiautoclave and details of its design and a method for automated synthesis of zeolites in said multiautoclave and, furthermore, application of the multiautoclave for an automated synthesis which is optimized simultaneously with regard to several synthesis parameters in the synthesis of zeolites. The multiautoclave consists typically of a pressure vessel/autoclave lined with an inert material with from 10 to 10,000 small, separated chambers, each typically having a volume of 0.2-2 ml, the chambers preferably being formed as through-going perforations in a central block and the perforations are sealed by means of balls, septa, stoppers or such which are placed at the bottom and top of each through-going perforation, and metal plates are placed over and under the Teflon plate so that the closing mechanism is pressed against the edges of the perforations in the Teflon plate with sufficient load to enable the chambers to be filled with aqueous mixtures and to be heated to 200 °C without the occurrence of leakage. Top-and bottom plates and closing mechanisms can be integrated so that all the perforations are sealed simultaneously when these are placed at the top and bottom sides of the central block.

MULTIAUTOCLOVE FOR COMBINATORIAL SYNTHESIS OF ZEOLITES AND OTHER MATERIALS

FIELD OF THE INVENTION

- 5 The present invention relates to a pressure and temperature reactor vessel, especially a multiautoclave and to details concerning the design of this equipment.

BACKGROUND OF THE INVENTION

Many materials, such as e.g. zeolites, are prepared by so-called hydrothermal synthesis at 10 temperatures ranging from 100°C to 200°C requiring crystallization times of 1 hour or more. For syntheses being carried out at temperatures that are higher than the solvent's boiling point, it is necessary to use pressure vessels, and these have to be suitable for the temperature and pressure used during the operation. The pressure vessel has to be designed so that the handling of it does not represent any unnecessary hazard, provided it 15 is used according to working instructions.

Zeolite syntheses are usually performed in strongly alkaline media, often at pH>14, and the reaction mixture will often contain toxic chemicals, such as e.g. fluoride. Conventionally, syntheses that may be performed at temperatures lower than 110°C are carried out in polymer bottles, often Teflon, while reactions at higher temperatures require 20 steel autoclaves, perhaps lined with Teflon. The price of an autoclave of this type with the required safety details are typically of the order of NOK 10.000,- or higher. Furthermore, such an autoclave will weigh from 1 kilogram and upwards, and all these elements represent limitations regarding the number of syntheses that may be performed in most laboratories in the course of one year.

25 Zeolite synthesis is often carried out by keeping the synthesis mixture at around 100°C for at least 6 h. At these moderate temperatures sealed chambers are necessary in order to avoid drying out of the synthesis mixture.

30 As an example of conventional zeolite synthesis, Zeolite Y can be prepared according to US 3.130.007, Example 1, by dissolving 5 g sodium aluminate containing 30 weight percent Na₂O and 44 weight percent Al₂O₃ and 22 g sodium hydroxide containing 77.5 weight percent Na₂O in 89,5 ml distilled water. This solution was added to 124.2 g of an aqueous colloidal silica sol with 29.5 weight percent SiO₂, so that the resulting mixture 35 had a composition corresponding to 13.9 Na₂O : Al₂O₃ : 28.2 SiO₂ : 471 H₂O, and the mixture was homogenized by stirring. The mixture was enclosed in a sealed glass vessel, placed in a water bath and heated at 100°C for 21 hours, after which the product was recovered by filtering, washed and dried. Common to all the synthesis procedures

redistribution of the substrates by transport through tubing back to the reaction chambers, and e) combination of a second portion of different composition to the first portions of molecules in the different reaction chambers in order to prepare new mixtures. This publication describes only a system for mixing and distribution of different molecules and not a system for hermetical sealing of the reaction chambers which would make it possible to operate at high temperatures, and this system would thus not be suitable for the synthesis of zeolites. In WO 96/11878 there is a description of extensive use of a combinatorial arrangement for synthesis of new materials, including zeolite synthesis at 100°C. Even though this patent application presents a detailed description of instrumentation and equipment developed for different purposes, autoclave systems required for performing the syntheses under the prevailing physical conditions (elevated pressure and temperatures exceeding 100°C) are not described.

Prior art teaches autoclaves with several chambers for special purposes, and there is for instance in US 5.505.916 a description of a metal cassette which can be opened and closed like a suitcase, and which has an interior with compartments intended for placement of the different instruments used by dentists, where these may be sterilized by autoclaving. Furthermore, large autoclaves intended for instance for the growth of crystals, are known, examples are described in US 5.322.591, US 5.312.506 and US 5.476.635, but the purpose of these and similar autoclaves is to make it possible to carry out large-scale syntheses, for which there is a great need when a synthetic procedure has been established and scale-up is desired, or when the purpose is to grow single crystals as large as possible. The autoclave described in the earlier mentioned US 5.312.506 is designed to withstand temperatures up to 1500°C for growth of crystals from metal melts. Another feature in connection with work with autoclaves is energy savings, and this is addressed in EP 0.434.890 A1, with description of a system for insulation of the autoclave walls and for the design of such insulating layers in the walls, which could be useful for large-scale autoclaving, but is of no relevance when working with small laboratory autoclaves which are heated in ovens.

Furthermore, there is a series of known equipment intended for synthesis of proteins and biopolymers, where the design comprises sheets with a large number of chambers intended for screening of syntheses and crystal growth, in its simplest form as described in US 5.096.676. US 5.400.741 describes a diffusion cell for growth of the largest and the most perfect crystals possible of macromolecular compounds by a technique called the "hanging drop" technique. Several patents, e.g. US 5.013.531, US 5.531.185, US 5.362.325 and EPA 0.553.539 A1, deal with cells for growth of proteins and biopolymer crystals in spacecrafts. Common for the latter patents is that the designs described are

1. Reduced size of the separate reaction chambers and increased number of reaction chambers what is called a multiautoclave.

This will lead to reduced use of reactants and thus cheaper synthesis.

2. Automated addition of reactants, for instance by having 100 reaction chambers present in one multiautoclave and by enabling this to be connected to a pipetting machine which makes quick and exact addition of all liquid reactants possible.

- 10 3. Simple and easy-to-use mechanism for the closing and opening of the multiautoclave.

4. Simple recovery and washing of the synthesis product and simple cleaning of the multiautoclave after use.

- 15 5. Devices allowing automated analysis with X-ray diffraction and automatic identification of known crystalline phases by combination of an automatic sample switcher, a structure library stored in a database and software that can monitor sample switching and identification.

Another objective of the present invention described here has been to design automated equipment for larger synthesis series and prepare formulations based on mixtures of different liquids/solutions with varying reactant ratios.

25 These and other objectives are attained by the present invention, which represents a breakthrough in terms of cost reduction for e.g. zeolite synthesis in that the reaction mixture crystallizes in a volume reduced typically to 1/100 of what has been used conventional, thereby achieving reduced consumption of reactants and cheaper syntheses, and further by enabling automated addition of reactants, e.g. by having 100 or more available reaction chambers in one single multiautoclave, and that the multiautoclave plates can be connected to a pipetting machine that makes quick and exact addition of all liquid reactants possible, and by being able to place several such plates with reaction chambers on top of each other without difficulty. Furthermore, an important feature of the present invention is the simple and not very time-consuming operation of the multiautoclave.

30 35 The present invention relates to a pressure and temperature reactor vessel comprising

in Figures 1 - 5. The thickness of the different plates and laminae may vary, always keeping in mind that a maximum number of small chambers with optimal size is desired, and that the chambers must be leak tight and dimensioned such that no excessive degree of deformation will take place under the operational conditions which the equipment is designed for. The central block consisting in a perforated plate (2), with a multitude of perforations, serve – when sandwiched between the plates (7a and 7b) and closed – as the frame of the pressure chambers, and may for use at higher temperatures (150 - 250°C) be made from stainless steel, aluminium, titanium or other rigid material s.a. PEEK or the like, with perforations of e.g. 10 mm diameters, where each perforation is lined with a segment of Teflon tubing or tubing made from another suitable polymer material, and where the walls of the linings e.g. can have a thickness of 1-3 mm. For use at temperatures below 150°C, the central block can be made entirely of Teflon, and for use below 130°C it can be made of polypropylene, and for use below 105°C it can be made of polyethylene. In the separate pressure chambers, balls (4) made from Teflon or other suitable material s.a. steel, PEEK, Nylon or glass may be used as a bottom- and top lid, also referred to as sealing means or septa (5) made from an elastomer or from another appropriate material s.a. Teflon in the shape of circular disks which will give the advantage in the form of reduced weight and volume. Septa should be made from an elastomer, preferably Viton, or other suitable material that can withstand temperatures of at least 200°C, and they may be equipped with Teflon lining (13) on the side facing the chamber as shown in Figures 4 and 5. Furthermore, said septa (5) should have a thickness considerably larger than the depth of immersion, as shown on Figure 3, in order to ensure a tight fit when assembling the different elements. As an alternative, septa or balls may be fastened on the bottom and top plates or on separate polymer films or a thin metal plate in such a way that they may be put in place and removed in a simple manner. The bottom and top plates (7) thus hold balls, septa, stoppers or other types of suitable cover means in place as the central block (2) is squeezed between the bottom and top plates. In order to avoid the use of balls, septa, stoppers or loose parts, the bottom and top plates can also be designed with a structure that has conical or hemispheric protrusions that fit into the perforations. Another design comprises polymer films moulded or otherwise shaped to cover all the perforations. In yet another design, the central block has been machined so that sharp edges (14) protrude around each perforation or well, as shown in Figure 5. The advantage of this design is that one smooth polymer sheet can be used as a lid or sealing device for all the chambers because the sharp protrusions cut into this polymer sheet so that leakage between adjacent chambers does not occur when the reaction vessel is closed with its locking mechanism. Said sharp protrusions (14) could alternatively consist of rings or e.g. a rectangular grid that are either welded onto the central block (2) or fastened by any other suitable method. These said protrusions may optionally be part of the insides

from the multiautoclave and into the perforations of another block which is made of a material suitable for performing calcination s.a. stainless steel or quartz.

Whenever the perforations, which on closing form the pressure chambers are going through the central block, the bottom has to be closed before charging with liquid or other reactants. This can be achieved in a simple manner by placing the perforated plate (2) on top of a plate (7a) with balls, septa or other sealing devices between them. The two plates (2 and 7a) are then bolted together with a set of bolts (9) with lengths somewhat less than the combined thickness of the two plates, so that no part of the bolts is protruding from the plate assembly. In the example shown in Figure 2, six bolts placed as illustrated have been found to be sufficient to hold the bottom plate sufficiently tight to the central block. After the chambers have been charged, the top plate (7b) with its sealing devices is put in place, and another set of bolts (11), which are considerably longer than the thickness of the entire multiautoclave, is put through a separate set of through-going holes (6) and tightened with nuts (12) at the bottom side with a torque wrench and with a load sufficient to keep the multiautoclave tight under the prevailing synthesis conditions it is going to be exposed to. Springs adjusted to a suitable pressure can, for instance, be put on the bolts before placing the nuts on them.

The advantages of the present invention are primarily related to the large rationalization gain that gives a correspondingly large economic saving. The saving is estimated to be from 90 to 99%. In other words, either the cost related to a given synthesis program is reduced by 90 - 99%, or it is possible for a given amount of money to perform 10 - 100 times as many syntheses. Such an automated layout will make it possible to perform e.g. 1000 syntheses/formulations simultaneously, and it will thus be very useful for all research laboratories, in industry as well as in research institutions/ universities.

Multiautoclaves suited for the purposes mentioned above might be designed as described in the following examples, but the descriptions are to be considered merely as examples of possible designs and the given measurements and other details shall not be considered to be limitations to the invention.

Example 1

A multiautoclave is built from 5 layers as shown in Figure 1. The different layers are placed on top of each other and bolted together so that 100 hermetically sealed chambers (1) are formed. By stacking several layers in a suitable way, it is possible to make a multiautoclave with, e.g. 1000 chambers or more. A decisive element in the invention described here is the combination of steel balls (4) and a thin polymer film (3) for the

also a set of 6 holes (10) with associated bolts (9) used to hold the bottom plate (7a) and the central block (2) together.

An upper aluminium plate (7b), 2 cm thick, is placed on top. This plate also has 9 smaller, through-going holes for bolts (11) used to keep all the plates bolted together.

In order to test the designed multiautoclave, the bottom plate (7a) and the central block (2) (Figure 3) were bolted together so that a plate with 100 wells and solid bottom embedding the septa (5) was formed. The resulting were each filled with 0.5 ml water, and a top plate with the associated septa was fastened to it by bolts. The multiautoclave was then placed in a heating cabinet at 150°C for three days. When the multiautoclave was opened after three days, the liquid levels in the 100 chambers were unchanged.

Example 3

In yet another embodiment, a heavy duty multiautoclave was designed and built essentially as shown in Figure 3, but in this case the 20 mm thick central block (2) was made of 316-stainless steel with 13.75 mm wells which were 19 mm deep. The remaining 1 mm of the plate was drilled through with a diameter of 12.45 mm resulting in a design, essentially, as displayed in Figure 4. The 13.75 mm perforations were lined with Teflon cylinders (13) with 2.75 mm wall thickness and 18 mm length so that above and below each cylinder there is a 1 mm deep recess with diameter 13.75 in one end and 12.45 in the other end. 3 mm thick Teflon disks with 13.75 mm and 12.45 mm diameters, respectively, (5) were used as bottom- and top lids for each of the small chambers.

Example 4

The bottom plate (7a) and the central block (2) of the multiautoclave described in Example 2 with septa (5) embedded were bolted together so that a plate with 100 wells with solid bottom was formed. This plate was then connected to an automatic pipetting machine of the "Tecan miniprepTM" type which was programmed to dispense the desired amounts from 4 different solutions to each of the 100 wells, so that a total of 100 reaction mixtures with different compositions was prepared in about 30 min.

Example 5

A multiautoclave as described in Example 1 was used for 64 zeolite syntheses based on 56 different gel compositions derived from 4 different solutions, including water, so that it covered the composition range for the Na - Si - Al system shown in Figure 6. The matrix had 64 points, but 8 of these were excluded because they appeared outside the desired range. The 8 spare chambers were instead used for reproductions, so that the total

TABLE I

| SiO ₂ /Al ₂ O ₃ | Na ₂ O/Al ₂ O ₃ | SiO ₂ /Na ₂ O | sum | SiO ₂ | Na ₂ O | Al ₂ O ₃ | H ₂ O |
|--|--|-------------------------------------|-------|------------------|-------------------|--------------------------------|------------------|
| 1.0 | 1.5 | 0.654 | 3.53 | 0.283 | 0.433 | 0.283 | 19.0 |
| 1.0 | 1.9 | 0.526 | 3.90 | 0.256 | 0.487 | 0.256 | 19.0 |
| 1.0 | 2.4 | 0.417 | 4.40 | 0.227 | 0.545 | 0.227 | 19.0 |
| 1.0 | 3.0 | 0.333 | 5.00 | 0.200 | 0.600 | 0.200 | 19.0 |
| 1.0 | 4.0 | 0.250 | 6.00 | 0.167 | 0.667 | 0.167 | 19.0 |
| 1.5 | 1.5 | 0.980 | 4.03 | 0.372 | 0.380 | 0.248 | 19.0 |
| 1.5 | 1.9 | 0.789 | 4.40 | 0.341 | 0.432 | 0.227 | 19.0 |
| 1.5 | 2.4 | 0.625 | 4.90 | 0.306 | 0.490 | 0.204 | 19.0 |
| 1.5 | 3.0 | 0.500 | 5.50 | 0.273 | 0.545 | 0.182 | 19.0 |
| 1.5 | 4.0 | 0.375 | 6.50 | 0.231 | 0.615 | 0.154 | 19.0 |
| 1.5 | 5.3 | 0.283 | 7.80 | 0.192 | 0.679 | 0.128 | 19.0 |
| 1.5 | 8.0 | 0.188 | 10.50 | 0.143 | 0.762 | 0.095 | 19.0 |
| 2.3 | 1.5 | 1.503 | 4.83 | 0.476 | 0.317 | 0.207 | 19.0 |
| 2.3 | 1.9 | 1.211 | 5.20 | 0.442 | 0.365 | 0.192 | 19.0 |
| 2.3 | 2.4 | 0.958 | 5.70 | 0.404 | 0.421 | 0.175 | 19.0 |
| 2.3 | 3.0 | 0.767 | 6.30 | 0.365 | 0.476 | 0.159 | 19.0 |
| 2.3 | 4.0 | 0.575 | 7.30 | 0.315 | 0.548 | 0.137 | 19.0 |
| 2.3 | 5.3 | 0.434 | 8.60 | 0.267 | 0.616 | 0.116 | 19.0 |
| 2.3 | 8.0 | 0.288 | 11.30 | 0.204 | 0.708 | 0.088 | 19.0 |
| 2.8 | 1.5 | 1.830 | 5.33 | 0.525 | 0.287 | 0.188 | 19.0 |
| 2.8 | 1.9 | 1.474 | 5.70 | 0.491 | 0.333 | 0.175 | 19.0 |
| 2.8 | 2.4 | 1.167 | 6.20 | 0.452 | 0.387 | 0.161 | 19.0 |
| 2.8 | 3.0 | 0.933 | 6.80 | 0.412 | 0.441 | 0.147 | 19.0 |
| 2.8 | 4.0 | 0.700 | 7.80 | 0.359 | 0.513 | 0.128 | 19.0 |
| 2.8 | 5.3 | 0.528 | 9.10 | 0.308 | 0.582 | 0.110 | 19.0 |
| 2.8 | 8.0 | 0.350 | 11.80 | 0.237 | 0.678 | 0.085 | 19.0 |
| 4.0 | 1.5 | 2.614 | 6.53 | 0.613 | 0.234 | 0.153 | 19.0 |
| 4.0 | 1.9 | 2.105 | 6.90 | 0.580 | 0.275 | 0.145 | 19.0 |
| 4.0 | 2.4 | 1.667 | 7.40 | 0.541 | 0.324 | 0.135 | 19.0 |
| 4.0 | 3.0 | 1.333 | 8.00 | 0.500 | 0.375 | 0.125 | 19.0 |
| 4.0 | 4.0 | 1.000 | 9.00 | 0.444 | 0.444 | 0.111 | 19.0 |
| 4.0 | 5.3 | 0.755 | 10.30 | 0.388 | 0.515 | 0.097 | 19.0 |
| 4.0 | 8.0 | 0.500 | 13.00 | 0.308 | 0.615 | 0.077 | 19.0 |
| 4.0 | 12.0 | 0.333 | 17.00 | 0.235 | 0.706 | 0.059 | 19.0 |
| 6.0 | 1.5 | 3.922 | 8.53 | 0.703 | 0.179 | 0.117 | 19.0 |
| 6.0 | 1.9 | 3.158 | 8.90 | 0.674 | 0.213 | 0.112 | 19.0 |
| 6.0 | 2.4 | 2.500 | 9.40 | 0.638 | 0.255 | 0.106 | 19.0 |
| 6.0 | 3.0 | 2.000 | 10.00 | 0.600 | 0.300 | 0.100 | 19.0 |
| 6.0 | 4.0 | 1.500 | 11.00 | 0.545 | 0.364 | 0.091 | 19.0 |
| 6.0 | 5.3 | 1.132 | 12.30 | 0.488 | 0.431 | 0.081 | 19.0 |
| 6.0 | 8.0 | 0.750 | 15.00 | 0.400 | 0.533 | 0.067 | 19.0 |
| 6.0 | 12.0 | 0.500 | 19.00 | 0.316 | 0.632 | 0.053 | 19.0 |
| 10.0 | 1.5 | 6.536 | 12.53 | 0.798 | 0.122 | 0.080 | 19.0 |
| 10.0 | 1.9 | 5.263 | 12.90 | 0.775 | 0.147 | 0.078 | 19.0 |
| 10.0 | 2.4 | 4.167 | 13.40 | 0.746 | 0.179 | 0.075 | 19.0 |
| 10.0 | 3.0 | 3.333 | 14.00 | 0.714 | 0.214 | 0.071 | 19.0 |
| 10.0 | 4.0 | 2.500 | 15.00 | 0.667 | 0.267 | 0.067 | 19.0 |
| 10.0 | 5.3 | 1.887 | 16.30 | 0.613 | 0.325 | 0.061 | 19.0 |
| 10.0 | 8.0 | 1.250 | 19.00 | 0.526 | 0.421 | 0.053 | 19.0 |
| 10.0 | 12.0 | 0.833 | 23.00 | 0.435 | 0.522 | 0.043 | 19.0 |
| 20.0 | 1.5 | 13.072 | 22.53 | 0.888 | 0.068 | 0.044 | 19.0 |
| 20.0 | 2.4 | 8.333 | 23.40 | 0.855 | 0.103 | 0.043 | 19.0 |
| 20.0 | 4.0 | 5.000 | 25.00 | 0.800 | 0.160 | 0.040 | 19.0 |
| 20.0 | 5.3 | 3.774 | 26.30 | 0.760 | 0.202 | 0.038 | 19.0 |
| 20.0 | 8.0 | 2.500 | 29.00 | 0.690 | 0.276 | 0.034 | 19.0 |
| 20.0 | 12.0 | 1.667 | 33.00 | 0.606 | 0.364 | 0.030 | 19.0 |

Example 6

In another embodiment, pre-mixed gels of aluminumphosphate, silicoaluminumphosphate and cobaltaluminumphosphate were prepared and administered by means of the "Tecan 5 Miniprep™" to the 100 cavities of the multiautoclave of example 3. Thereafter 6 different organic compounds were added according to the molar ratios specified in Table 3. The multiautoclave was then closed and was heated for 48 h in an oven at 200°C. The solid synthesis products were recovered as described in example 5 and were dried overnight at ambient temperatures. The products were characterised by X-ray diffraction using a 10 Siemens D-5000 diffractometer equipped with PSD detector and an automatic sample shifter. Several different crystalline phases were identified among the products including those of the structures AFI, ERI and CHA.

Table 3, gel compositions for MeAPO syntheses, continued.

| Position | Mols AlPO gel | Mols SAPO gel | Mols CoAPO gel | R1 | Mols R1 | R2 | Mols R2 |
|----------|---------------|---------------|----------------|-----------|---------|-----------|---------|
| 50 | 0 | 0.5 | 0.5 | TRIPROPYL | 1 | - | 0 |
| 51 | 0 | 0.75 | 0.25 | TRIPROPYL | 1 | - | 0 |
| 52 | 0 | 0.25 | 0.75 | DI-N-PROP | 1 | - | 0 |
| 53 | 0 | 0.5 | 0.5 | DI-N-PROP | 1 | - | 0 |
| 54 | 0 | 0.75 | 0.25 | DI-N-PROP | 1 | - | 0 |
| 55 | 0 | 0.25 | 0.75 | TEAOH | 1 | - | 0 |
| 56 | 0 | 0.5 | 0.5 | TEAOH | 1 | - | 0 |
| 57 | 0 | 0.75 | 0.25 | TEAOH | 1 | - | 0 |
| 58 | 0 | 0.25 | 0.75 | TRIETHYLA | 1 | - | 0 |
| 59 | 0 | 0.5 | 0.5 | TRIETHYLA | 1 | - | 0 |
| 60 | 0 | 0.75 | 0.25 | TRIETHYLA | 1 | - | 0 |
| 61 | 0 | 0 | 1 | CYCLOHEXY | 0.25 | MORPHOLIN | 0.75 |
| 62 | 0 | 0 | 1 | CYCLOHEXY | 0.25 | TRIPROPYL | 0.75 |
| 63 | 0 | 0 | 1 | CYCLOHEXY | 0.25 | DI-N-PROP | 0.75 |
| 64 | 0 | 0 | 1 | CYCLOHEXY | 0.25 | TEAOH | 0.75 |
| 65 | 0 | 0 | 1 | CYCLOHEXY | 0.25 | TRIETHYLA | 0.75 |
| 66 | 0 | 0 | 1 | MORPHOLIN | 0.25 | TRIPROPYL | 0.75 |
| 67 | 0 | 0 | 1 | MORPHOLIN | 0.25 | DI-N-PROP | 0.75 |
| 68 | 0 | 0 | 1 | MORPHOLIN | 0.25 | TEAOH | 0.75 |
| 69 | 0 | 0 | 1 | MORPHOLIN | 0.25 | TRIETHYLA | 0.75 |
| 70 | 0 | 0 | 1 | TRIPROPYL | 0.25 | DI-N-PROP | 0.75 |
| 71 | 0 | 0 | 1 | TRIPROPYL | 0.25 | TEAOH | 0.75 |
| 72 | 0 | 0 | 1 | TRIPROPYL | 0.25 | TRIETHYLA | 0.75 |
| 73 | 0 | 0 | 1 | DI-N-PROP | 0.25 | TEAOH | 0.75 |
| 74 | 0 | 0 | 1 | DI-N-PROP | 0.25 | TRIETHYLA | 0.75 |
| 75 | 0 | 0 | 1 | TEAOH | 0.25 | TRIETHYLA | 0.75 |
| 76 | 0 | 0 | 1 | CYCLOHEXY | 0.75 | MORPHOLIN | 0.25 |
| 77 | 0 | 0 | 1 | CYCLOHEXY | 0.75 | TRIPROPYL | 0.25 |
| 78 | 0 | 0 | 1 | CYCLOHEXY | 0.75 | DI-N-PROP | 0.25 |
| 79 | 0 | 0 | 1 | CYCLOHEXY | 0.75 | TEAOH | 0.25 |
| 80 | 0 | 0 | 1 | CYCLOHEXY | 0.75 | TRIETHYLA | 0.25 |
| 81 | 0 | 0 | 1 | MORPHOLIN | 0.75 | TRIPROPYL | 0.25 |
| 82 | 0 | 0 | 1 | MORPHOLIN | 0.75 | DI-N-PROP | 0.25 |
| 83 | 0 | 0 | 1 | MORPHOLIN | 0.75 | TEAOH | 0.25 |
| 84 | 0 | 0 | 1 | MORPHOLIN | 0.75 | TRIETHYLA | 0.25 |
| 85 | 0 | 0 | 1 | TRIPROPYL | 0.75 | DI-N-PROP | 0.25 |
| 86 | 0 | 0 | 1 | TRIPROPYL | 0.75 | TEAOH | 0.25 |
| 87 | 0 | 0 | 1 | TRIPROPYL | 0.75 | TRIETHYLA | 0.25 |
| 88 | 0 | 0 | 1 | DI-N-PROP | 0.75 | TEAOH | 0.25 |
| 89 | 0 | 0 | 1 | DI-N-PROP | 0.75 | TRIETHYLA | 0.25 |
| 90 | 0 | 0 | 1 | TEAOH | 0.75 | TRIETHYLA | 0.25 |

91-100 Reproductions chosen at random from compositions 1 - 90

CYCLOHEX = Cyclohexylamine

MORPHOLI = morpholine

TRIPROPYL = tripropylamine

DI-N-PROP = dipropylamine

TEAOH = tetraethylammonium hydroxide

TRIETHYLA = triethylamine

the cover means, such that they present a curved surface towards the opening of the multitude of perforations in the central block.

9. A pressure and temperature reactor vessel as claimed in claim 1, wherein the sealing means consists of circular disks or other similar circular-shaped components that may be permanently fastened to the cover means.

10. A pressure and temperature reactor vessel as claimed in claim 1, wherein the sealing means consists of circular disks or other similar circular-shaped components that may be loosely fastened to the cover means.

11. A pressure and temperature reactor vessel as claimed in claim 1, wherein the sealing means consists of a flat plate or membrane, covering all the chambers, that may be permanently fastened to the cover means.

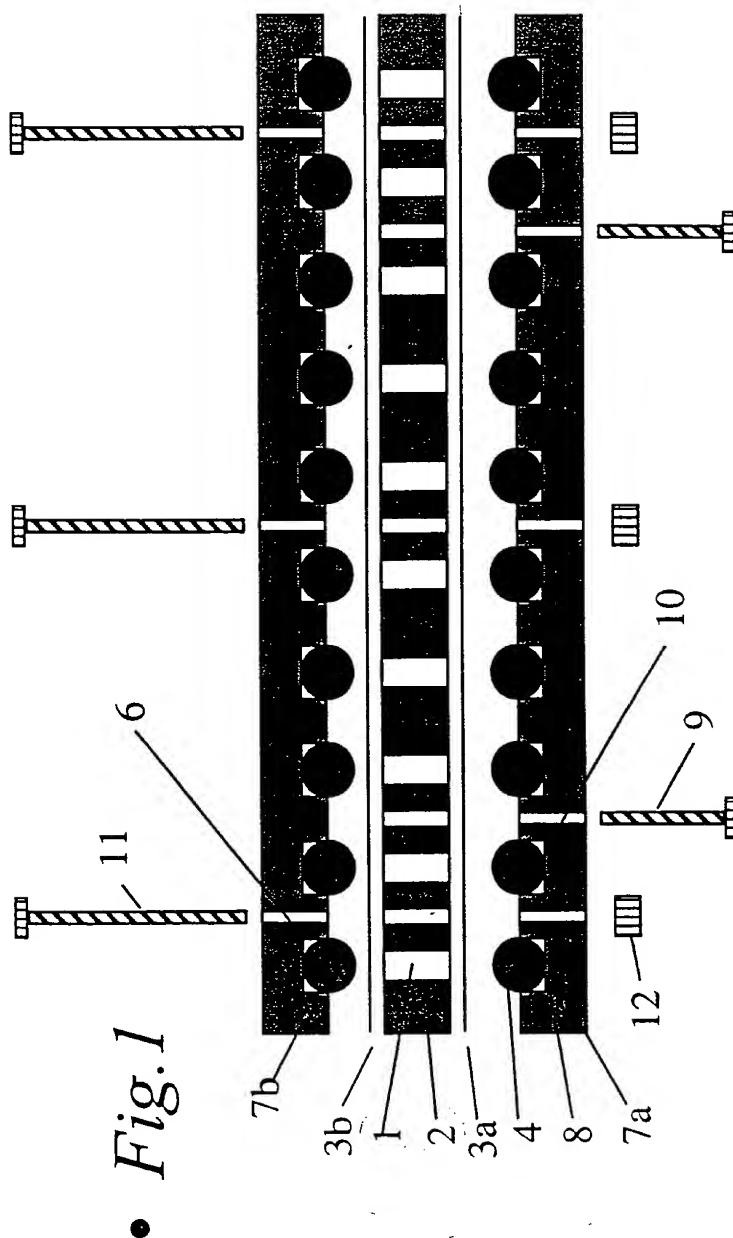
15 12. A pressure and temperature reactor vessel as claimed in claim 1, wherein the sealing means consists of a flat plate or membrane, covering all the chambers, that may be loosely fastened to the cover means.

20 13. A pressure and temperature reactor vessel as claimed in claim 1, wherein said locking means acts in concert with a single cover means on one surface of the central block to define a multitude of cavities.

25 14. A pressure and temperature reactor vessel as claimed in claim 1, wherein said locking means consists of a plurality of fasteners passing by means of appropriate holes from the upper surface of the upper cover means through the central block through to the lower surface of the lower cover means.

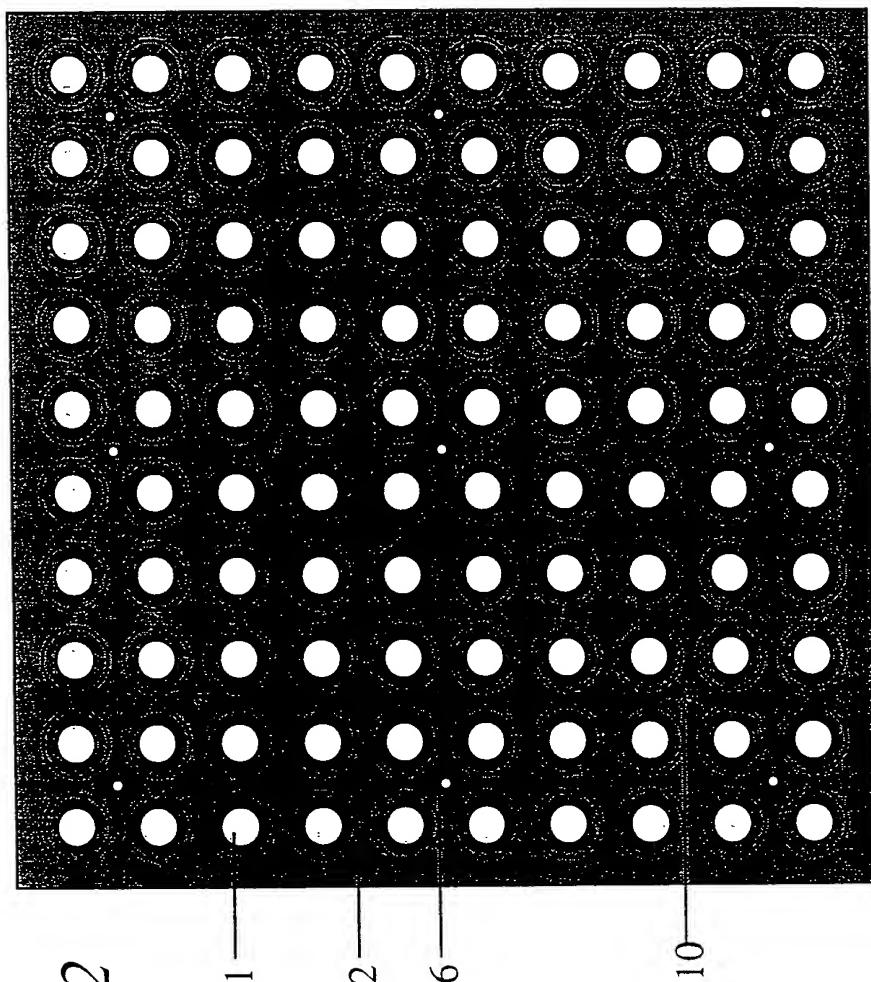
30 15. A pressure and temperature reactor vessel as claimed in claim 1, wherein said cover means is a rigid flat plate.

35 16. A pressure and temperature reactor vessel as claimed in claim 1, wherein said cover means, acting in concert with the sealing means, has a multitude of protruding profiles of dimensions sufficiently larger than the dimensions of the perforations in the central block and of cross sectional shape such that in concert with the sealing means through the action of the locking means, a pressure tight seal is formed over and around each of the multitude of perforations in the central block.

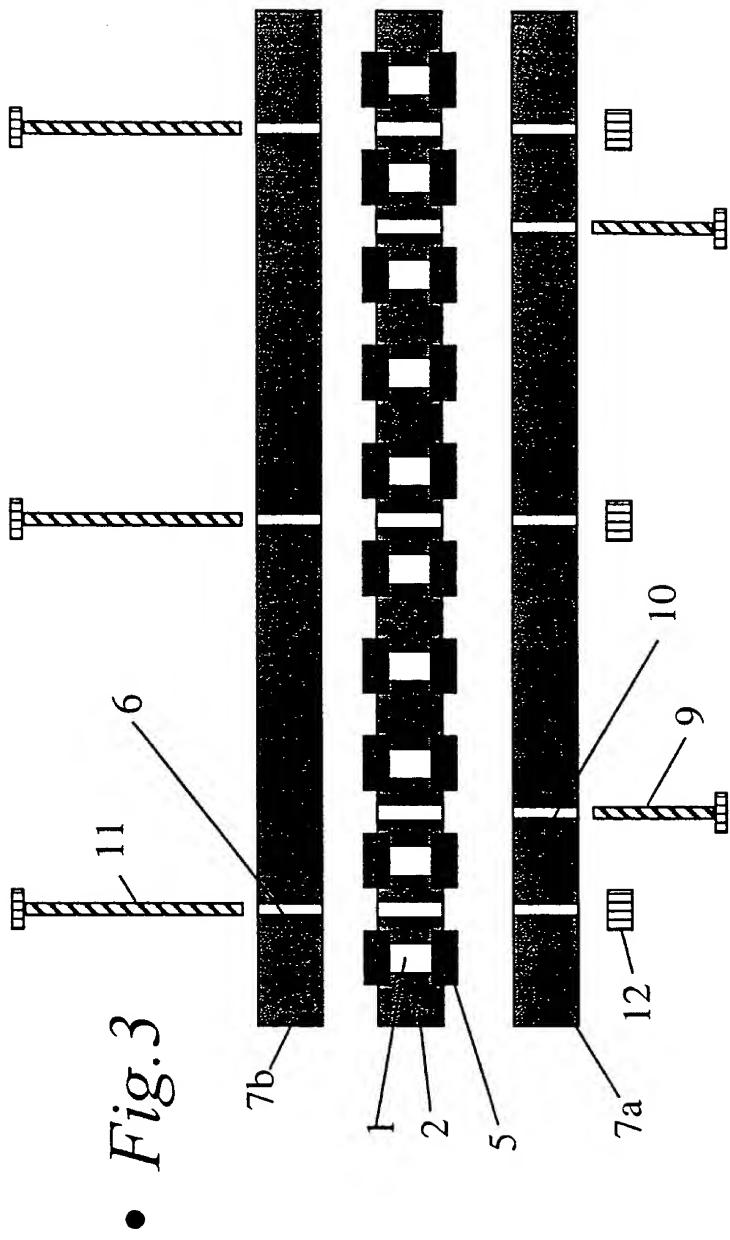


• Fig. 1

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• Fig. 2



• Fig. 3

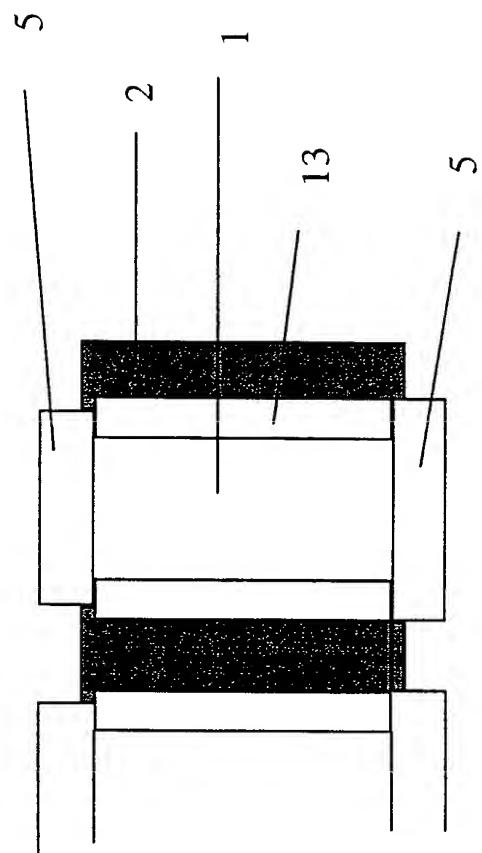
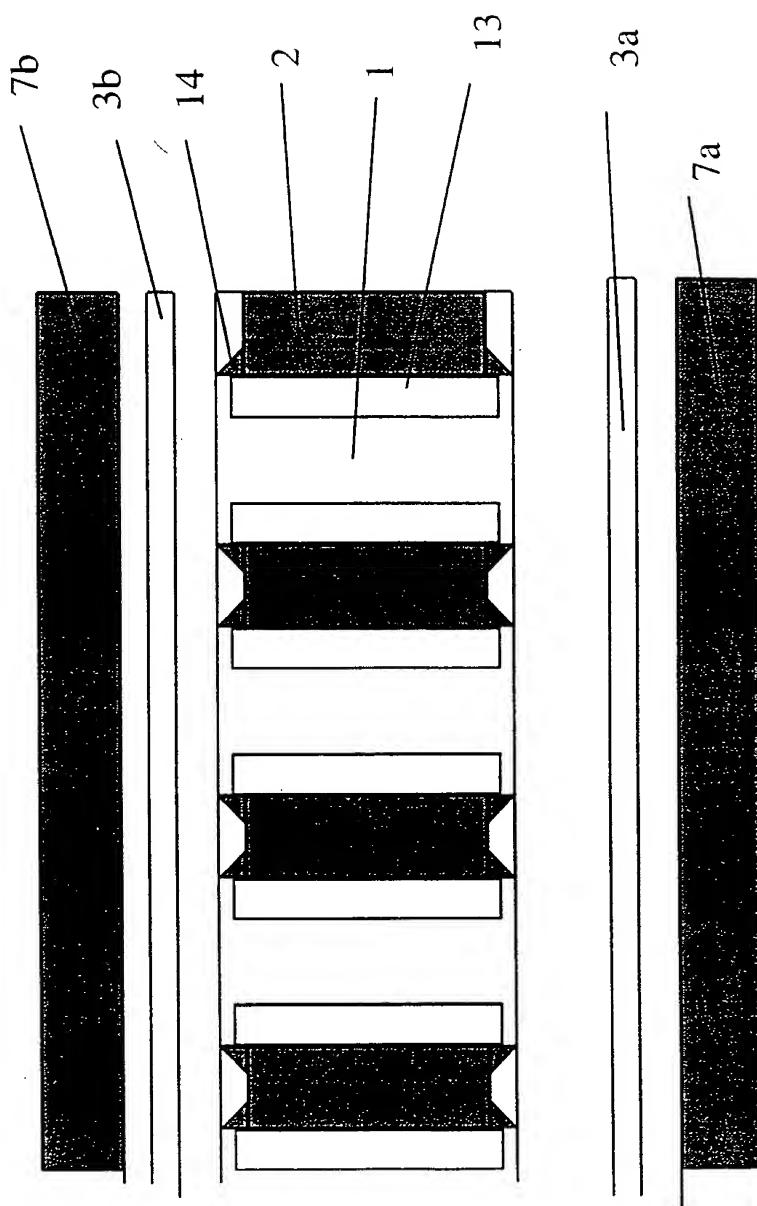


Fig. 4

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Fig 5a

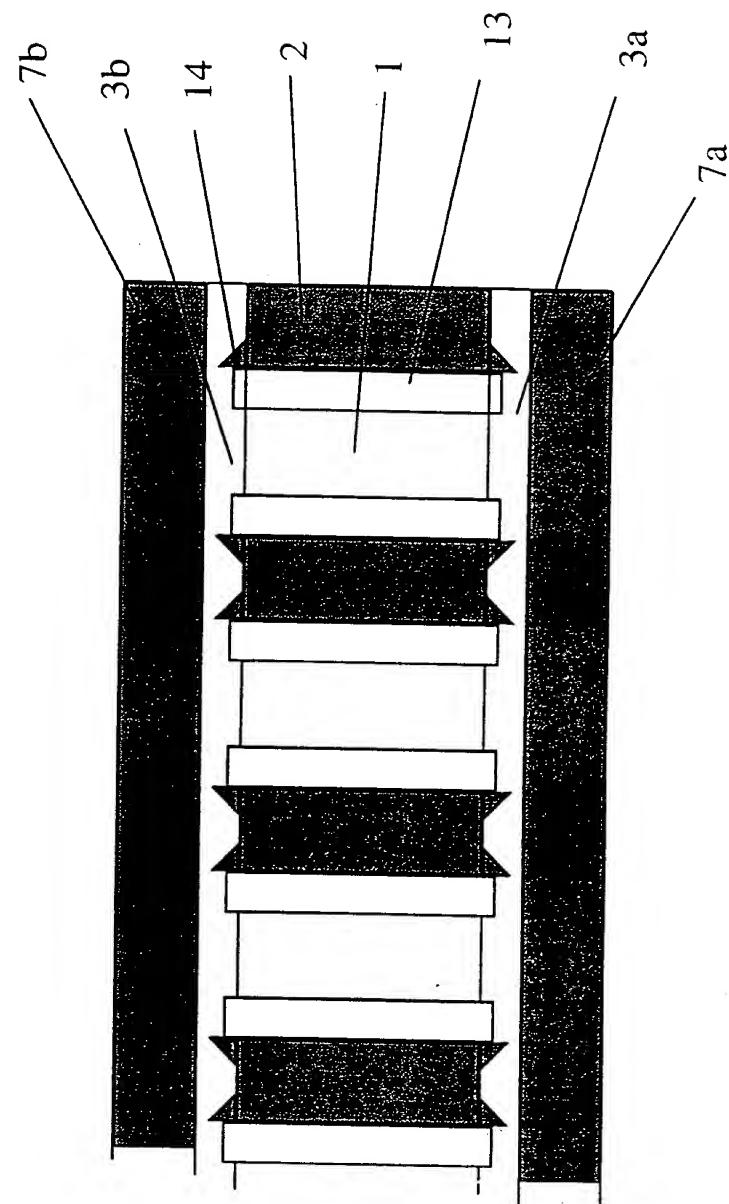
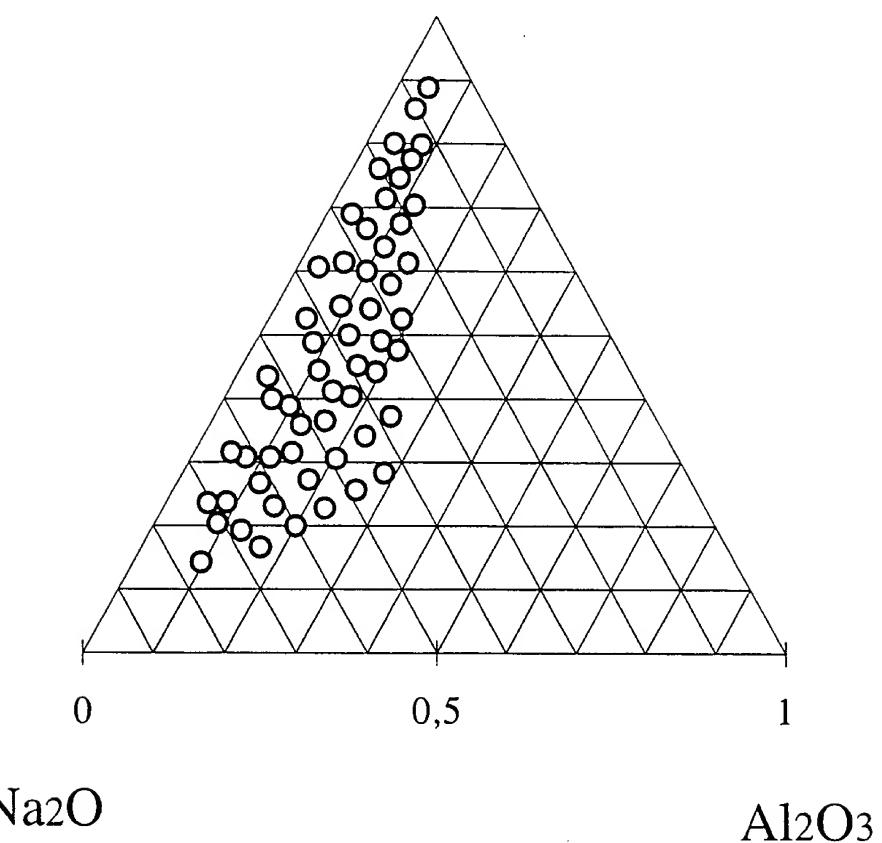


Fig. 5b

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Fig. 6
SiO₂



INTERNATIONAL SEARCH REPORT

International application No.

PCT/NO 98/00051

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: B01J 3/00, C30B 29/34

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: B01J, C01B, C30B, F17C, F16J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|-----------|--|-----------------------|
| Y | US 5112574 A (NIKKI HORTON), 12 May 1992 (12.05.92), column 3, line 65 - column 4, line 4, figures 1-4,9, abstract -- | 1-17 |
| Y | US 5505916 A (BERNIE B. BERRY, JR.), 9 April 1996 (09.04.96), column 6, line 3 - line 7, figure 1 -- | 1-17 |
| A | US 5400741 A (GEORGE T. DETITTA ET AL), 28 March 1995 (28.03.95), figures 1-7 -- | 1-17 |
| A | US 5531185 A (KOJI ASANO ET AL), 2 July 1996 (02.07.96), figures 8-9, abstract -- | 1-12 |

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Date of the actual completion of the international search

12 June 1998

Date of mailing of the international search report

30-06-1998

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INTERNATIONAL SEARCH REPORT
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